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Energy levels of the weakly interacting radicals

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Abstract. Energy levels of the weakly interacting radicals are estimated on the basis of planar methyl radical interaction as a model. These levels depend on the given separation r between the centers of mass. The appropriate Schrödinger equation is solved by using the Brillouin–Wigner series method. Analytical forms for the integrals used to estimate matrix elements are derived. The principle of total momentum conservation is strictly obeyed. Some energy levels cannot be estimated as a result of divergence.

Key words: Methyl radical recombination – Energy levels

1 Introduction

In this work we are concerned with the systems that feature interactions weak enough to justify an assumption of the potential energy treated as a perturbation [1]. Van der Waals forces are well known to belong to such systems [2]. Interaction between the recombining radicals are also very weak, described by a loose transition state [3, 4]. The active centers separation corresponds frequently to van der Waals distances for many molecules [4]. Calculus, employing a simple Rayleigh–Schrödinger series, was also used in studies of ion–molecule reaction kinetics [5, 6].

Interaction energy of methyl radicals is chosen as our model. Our description is based mostly on the model developed by Wardlaw and Marcus [7]. According to the WM model the reacting radicals are treated as the interacting quasi-rigid bodies. The degrees of freedom are subdivided into conserved and transitional ones. The conserved vibrations do not change practically their form of motion during the approach along the given separation r between the centers of mass (reaction coordinate), while the free rotations of the reactants and their relative orbital motion do. The potential for the transitional degrees of freedom incorporates nonbonded and bonded interactions [7].

This model was found to offer the best reproduction of recombination kinetics experimental data [7, 8].

A Brillouin–Wigner series is used for the estimation of energy levels of our interacting systems [9]; generally, adiabatic approximation is employed [10].

Energy of the interacting systems is represented as a total of electronic, vibrational and rotational contributions. Coupling between total angular momentum and internal momentum as well as other couplings are not taken into account. However, such corrections are feasible and can be worked out were such a need to arise.

The results obtained in this work are used to investigate an important initial stage of radical recombination at higher pressures and temperatures [11].

2 Definition of basic values

In the interacting systems treated as the quasi-rigid bodies the part of the Hamiltonian describing motion at the given separation r between the centers of mass can be singled out. This partial Hamiltonian can be written in the form

$$\hat{H}_J = \hat{H}_{\text{rot1}} + \hat{H}_{\text{rot2}} + \hat{H}_{\text{orb}} + V, \tag{1}$$

where $\hat{H}_{\text{rot1}}$ and $\hat{H}_{\text{rot2}}$ are the operators of the kinetic energy of the intrinsic rotational energy for the two interacting components, respectively; $\hat{H}_{\text{orb}}$ is the operator of the orbital energy, and V is the potential. The subscript J denotes the total momentum of the system. The distance r in $\hat{H}_J$ is the parameter to be varied.

The problem for quantum mechanics is to solve the Schrödinger equation with Hamiltonian $\hat{H}_J$,

$$\hat{H}_J \psi_n^{\text{JM}} = E_n(r) \psi_n^{\text{JM}}. \tag{2}$$

Equation (2) is a part of the complete equation that incorporates the term describing motion of the interacting systems along r. Solutions to Eq. (2) can be used as a base to find solutions both in adiabatic and non-adiabatic approximations [11].

As the principle of total momentum conservation in the system has to be obeyed, only those functions ψ_n^{JM} solving Eq. (2) can be accepted which belong to the class Q (means the one which is continuous, finite and single valued for all values of variables) and fulfill explicitly the rules of momentum addition in quantum mechanics. The methods used to solve Eq. (2) and calculations of the matrix elements are general and can be used to investigate various systems.

The two methyl radicals are labeled with the subscripts 1 and 2, respectively. Rotational motion of radicals is described by using the Euler angles α, β and γ. Definition of these angles and description of the location of radicals is given in Ref. [12]. Throughout, the designations and symbols used are those from Ref. [13].

Since the radicals are rotors of the oblate symmetric top type, the operator for the kinetic energy of the first radical is written in the form [13]

$$\hat{H}_{\text{rot1}} = A_1 \hat{J}_1^2 + \hat{J}_{z1}^2 (B_1 - A_1), \tag{3}$$

where

$$A_1 = \frac{\hbar^2}{2I_x} \tag{4}$$

$$B_1 = \frac{\hbar^2}{2I_z} \tag{5}$$

$\hat{J}_1$ and $\hat{J}_{z1}$ are angular momentum operators for molecule 1, referred to molecule-fixed axis, quantized with numbers j_1 and k_1, respectively. The moments of inertia are $I_z = 5.8 \times 10^{-47}$ kg m^2 and $I_x = 2.9 \times 10^{-47}$ kg m^2 ($I_y = I_x$). If the second radical is to be considered, the subscripts 1 and 2 have to be interchanged.

The third component of Hamiltonian 1 describes the energy of mutual orbital motion. It is given by [13]

$$\hat{H}_{\mathrm{orb}} = \frac{\hbar^2}{2\mu r^2}\hat{L}^2, \tag{6}$$

where μ is the reduced mass of the system and $\hat{L}$ is the operator of the orbital motion in the spherical coordinates r, θ and ϕ quantized with number l.

The last component of Hamiltonian 1 is the potential of interaction of two planar methyl radicals. Search for the analytical form of this potential is a problem in itself addressed in Ref. [12]. Approximation is based on the *ab initio* results of Darvesh et al. [8]. At the distance $r > 3.5$ Å this potential can be simplified to the form [12]

$$\begin{aligned} V = {} & \varepsilon_0 - \varepsilon_1 \cos^2\theta_1 - \varepsilon_2 \cos^2\theta_2 \\ & - A \exp\left(-\frac{Zr}{a_0}\right)[f_1(r)\cos\theta_{12} \\ & - f_2(r)\cos\theta_1\cos\theta_2]^2, \end{aligned} \tag{7}$$

where

$$\cos\theta_1 = \cos\beta_1\cos\theta + \sin\beta_1\sin\theta\cos(\alpha_1 - \phi), \tag{8}$$

$$\cos\theta_2 = \cos\beta_2\cos\theta + \sin\beta_2\sin\theta\cos(\alpha_2 - \phi), \tag{9}$$

$$\cos\theta_{12} = \cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos(\alpha_1 - \alpha_2), \tag{10}$$

$$f_1(r) = 1 + \tfrac{1}{15}a[15 + a(6 + a)], \tag{11}$$

$$f_2(r) = a^2\tfrac{1}{5}[1 + a(1 + \tfrac{1}{3}a)], \tag{12}$$

$$a = \frac{Zr}{2a_0}. \tag{13}$$

The coefficients ε_0, ε_1 and ε_2 are composite functions of r and, moreover, depend on some values characteristic for the interaction. The representative values for these coefficients for the selected r's as well as the values for some other coefficients are assembled in Table 1.

To estimate the energy levels $E_n(r)$ approximate methods of quantum mechanics have to be applied. Thus $\hat{H}_J$ is transformed into

$$\hat{H}_J = \hat{H}_J^{(0)} + \hat{H}', \tag{14}$$

where

$$\hat{H}_J^{(0)} = \hat{H}_{\mathrm{rot1}} + \hat{H}_{\mathrm{rot2}} + \hat{H}_{\mathrm{orb}} + \varepsilon_0 \tag{15}$$

and

$$\hat{H}' = V - \varepsilon_0. \tag{16}$$

Hamiltonian $\hat{H}_J^{(0)}$ describes the rotational motion of radicals in the field of mutual interaction. The ε_0 potential is spherically symmetrical.

Table 1. Selected values for the parameters of potential V [3][a]

$r/\text{Å}$	$f_1(r)$	$f_2(r)$	$-A\exp(-2a)$	ε_0 [kcal/mol]	ε_1 [kcal/mol]
3.5	90.98	599.2	-8.607×10^{-6}	0.0225	0.1528
3.7	104.1	736.4	-3.078×10^{-6}	−0.2135	0.0508
4.0	126.1	984.6	-6.580×10^{-7}	−0.2968	−0.0091
4.2	142.4	1182	-2.353×10^{-7}	−0.2824	−0.0216
4.5	169.4	1531	-5.030×10^{-8}	−0.2321	−0.0248
5.0	221.6	2279	-3.845×10^{-9}	−0.1485	−0.0182
5.5	283.7	3272	-2.939×10^{-10}	−0.0911	−0.0112
6.0	356.4	4558	-2.247×10^{-11}	−0.0559	−0.0066
7.0	537.3	8227	-1.313×10^{-13}	−0.0222	−0.0022

[a] $Z=2.7212$; $A=564.25$ kcal/mol

Solutions to the Schrödinger equation (17) with Hamiltonian (15) are known [13]:

$$\hat{H}_J^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}. \tag{17}$$

Taking into account the principle of total momentum conservation wavefunctions $\psi_n^{(0)}$ can be written in the form

$$\psi_n^{(0)} = N\sum_{m_l m_j}\left(\begin{array}{cc|c} l & j & J \\ m_l & m_j & M \end{array}\right)\sum_{m_1 m_2}\left(\begin{array}{cc|c} j_1 & j_2 & j \\ m_1 & m_2 & m_j \end{array}\right) D^{j_1}_{m_1 k_1} D^{j_2}_{m_2 k_2} Y_{l,m_1}. \tag{18}$$

The symbol $D^{j_1}_{m_1 k_1}$ is the generalized spherical function describing the rotational motion of the first radical, while m_1 is the projection of j_1 on the fixed axis $x'_{(1)}$ [12]. Analogous notation refers to the second radical. The symbol $Y_{l,m_l}(\theta,\phi)$ is the wave function, spherical harmonic, describing the orbital motion of radicals [13]; m_l is the projection of l on the fixed axis in the center of mass frame. The symbol j denotes addition of j_1 and j_2. It takes on the values within the interval $|j_1-j_2|\leqslant j\leqslant j_1+j_2$; m_j is its projection and is equal to $m_j=m_1+m_2$. Thus, the total momentum J can take on the values $|l-j|\leqslant J\leqslant l+j$ while $M=m_l+m_j$.

The symbols $\left(\begin{smallmatrix} j_1 & j_2 & | & j \\ m_1 & m_2 & | & m_j \end{smallmatrix}\right)$ are the coefficients for expansion of the states determined by the numbers $|j,m_j\rangle$ into the states $|j_1,m_1\rangle|j_2,m_2\rangle$, called the Clebsch–Gordan coefficients [13]. Similarly, the symbols $\left(\begin{smallmatrix} l & j & | & J \\ m_l & m_j & | & M \end{smallmatrix}\right)$ are the coefficients for expansion of the states $|J,M\rangle$ into the states $|j,m_j> Y_{l,m_l}$. A quantity

$$N=\left(\frac{2j_1+1}{8\pi^2}\frac{2j_2+1}{8\pi^2}\right)^{1/2} \tag{19}$$

is the normalization coefficient determined on the basis of the condition for orthogonality and normalization of spherical functions and spherical harmonics [13]. Thus, the symbol n denotes the set of quantum numbers $n\equiv\{j_1,j_2,j,l,J,k_1,k_2\}$. The energy levels $E_n^{(0)}$ are given by

$$E_n^{(0)} = A_1 j_1(j_1+1) + (B_1-A_1)k_1 + A_2 j_2(j_2+1) + (B_2-A_2)k_2 + \frac{\hbar}{2\mu r^2}l(l+1) + \varepsilon_0. \tag{20}$$

Inspection of Table 1 shows that the radial part of potential V, i.e. $\hat{H}'$, decreases markedly with increasing r. The decrease in the last term of Eq. (7) is especially pronounced. Apparently, for some range r the dependence on the orientation becomes a small perturbation with respect to $\hat{H}_J^{(0)}$. If so, solutions to Eq. (18) are a natural basis for calculations.

The matrix elements of the type shown below as Eq. (21) have to be estimated:

$$V_{nm} = \int \cdots \int \psi_n^{(0)} \hat{H}' \psi_m^{(0)}\, d\tau \equiv (\psi_n^{(0)}, \hat{H}' \psi_m^{(0)}), \tag{21}$$

$d\tau$ is the element of volume and the limit of integration extends over the whole range of variability [13]. The symbol m denotes the set of quantum numbers $\{j_1', j_2', j', l', J, k_1, k_2\}$ that is equal or unequal to n. Estimation of these integrals follows in the next section.

3 Estimation of matrix elements

Matrix element given in Eq. (21) can be written as

$$\begin{aligned} V_{nm} = &-\varepsilon_1(\psi_n^{(0)}, \cos^2\theta_1 \psi_m^{(0)}) - \varepsilon_2(\psi_n^{(0)}, \cos^2\theta_2 \psi_m^{(0)}) - A\exp(-Zr/a_0) \\ &\times (\psi_n^{(0)}, [f_1(r)\cos\theta_{12} - f_2(r)\cos\theta_1\cos\theta_2]^2 \psi_m^{(0)}) \end{aligned} \tag{22}$$

and can be evaluated using the well-known formula for the operator-products [10]

$$(\psi_n^{(0)}, \hat{F}\hat{K}\psi_m^{(0)}) = \sum_{m'} (\psi_n^{(0)}, \hat{F}\psi_{m'}^{(0)})(\psi_{m'}^{(0)}, \hat{K}\psi_m^{(0)}). \tag{23}$$

For instance,

$$(\psi_n^{(0)}, \cos^2\theta_{12}\psi_m^{(0)}) = \sum_{m'} (\psi_n^{(0)}, \cos\theta_{12}\psi_{m'}^{(0)})(\psi_{m'}^{(0)}, \cos\theta_{12}\psi_m^{(0)}). \tag{24}$$

To estimate the matrix element, V_{nm}, the integrals $(\psi_n^{(0)}, \cos\theta_1\psi_m^{(0)})$, $(\psi_n^{(0)}, \cos\theta_2\psi_m^{(0)})$ and $(\psi_n^{(0)}, \cos\theta_{12}\psi_m^{(0)})$ have to be calculated. One more notation is useful to describe the relations between the sets n and m. Let us consider the integral for which $j_1' = j_1 + 1$, $j_2' = j_2 - 1$ $(j_2 > 0)$:

$$\begin{aligned} &\langle j_1+1, j_2-1, j, l | \cos\theta_{12} | j_1, j_2, j, l \rangle \\ &= \left(\frac{2j_1+1}{8\pi^2}\frac{2j_2+1}{8\pi^2}\right)^{1/2} \left(\frac{2j_1+3}{8\pi^2}\frac{2j_2-1}{8\pi^2}\right)^{1/2} \sum_{m_l m_j} \left(\begin{array}{cc|c} l & j & J \\ m_l & m_j & M \end{array}\right) \sum_{m_1 m_2} \left(\begin{array}{cc|c} j_1 & j_2 & j \\ m_1 & m_2 & m_j \end{array}\right) \\ &\times \sum_{m_l' m_j'} \left(\begin{array}{cc|c} l & j & J \\ m_l' & m_j' & M \end{array}\right) \sum_{m_1' m_2'} \left(\begin{array}{cc|c} j_1+1 & j_2-1 & j \\ m_1' & m_2' & m_j' \end{array}\right) \\ &\times \int \cdots \int D^{*j_1+1}_{m_1'k_1'} D^{*j_2-1}_{m_2'k_2'} Y^*_{l', m_l'} \cos\theta_{12} D^{j_1}_{m_1k_1} D^{j_2}_{m_2k_2} Y_{l, m_l}\, d\tau. \end{aligned} \tag{25}$$

The numbers J, k_1 and k_2 are the same on both sides of the operator and, consequently, do not feature in this notation. As the total momentum is conserved, all the matrix elements for which $J' \neq J$ vanish.

Recurrent expressions [13] are needed for further calculations. For example,

$$\cos\beta_1 D^{j_1}_{m_1 k_1} = \frac{a(j_1, m_1, k_1)}{2j_1+1} D^{j_1-1}_{m_1 k_1} + \frac{m_1 k_1}{j_1(j_1+1)} D^{j_1}_{m_1 k_1} + \frac{a(j_1+1, m_1, k_1)}{2j_1+1} D^{j_1+1}_{m_1 k_1}, \tag{26}$$

where

$$a(j_1, m_1, k_1) = \frac{\sqrt{(j_1^2 - m_1^2)(j_1^2 - k_1^2)}}{j_1}. \tag{27}$$

In other cases the procedure is similar [13].

Further procedure involves substitution from Eqs. (26) and (27), etc., into Eq. (25). Integration and summation over m_l', m_j', m_1' and m_2' yields ultimately

$$\begin{aligned}
&\langle j_1+1, j_2-1, j, l \,|\cos\theta_{12}|\, j_1, j_2, j, l\rangle \\
&= \left(\frac{2j_1+1}{2j_1+3}\,\frac{2j_2+1}{2j_2-1}\right)^{1/2} \sum_{m_l m_j} \left(\begin{array}{cc|c} l & j & J \\ m_l & m_j & M \end{array}\right)^2 \sum_{m_1 m_2} \left(\begin{array}{cc|c} j_1 & j_2 & j \\ m_1 & m_2 & m_j \end{array}\right) \\
&\quad\times\left\{\left(\begin{array}{cc|c} j_1+1 & j_2-1 & j \\ m_1 & m_2 & m_j \end{array}\right) \frac{a(j_1+1, m_1, k_1)}{2j_1+1}\,\frac{a(j_2, m_2, k_2)}{2j_2+1}\right. \\
&\quad+\frac{1}{2}\left(\begin{array}{cc|c} j_1+1 & j_2-1 & j \\ m_1+1 & m_2-1 & m_j \end{array}\right) \frac{b(j_1+1, m_1+1, k_1)}{2j_1+1}\,\frac{b(j_2, m_2, k_2)}{2j_2+1} \\
&\quad\left.+\frac{1}{2}\left(\begin{array}{cc|c} j_1+1 & j_2-1 & j \\ m_1-1 & m_2+1 & m_j \end{array}\right) \frac{b(j_1+1, -m_1+1, k_1)}{2j_1+1}\,\frac{b(j_2, -m_2, k_2)}{2j_2+1}\right\},
\end{aligned} \tag{28}$$

where

$$b(j_1, m_1, k_1) = \frac{\sqrt{(j_1+m_1)(j_1+m_1-1)(j_1^2 - k_1^2)}}{j_1}. \tag{29}$$

Integral (28) is further transformed using the system of transformations and recurrencies for the Clebsch–Gordan coefficients

$$\left(\begin{array}{cc|c} j_1+1 & j_2-1 & j \\ m_1 & m_2 & m_j \end{array}\right) = (-1)^{j_1+1-m_1} \left(\frac{2j+1}{2j_2-1}\right)^{1/2} \left(\begin{array}{cc|c} j & j_1+1 & j_2-1 \\ m_j & -m_1 & m_2 \end{array}\right) \tag{30}$$

followed by

$$\begin{aligned}
&\left(\begin{array}{cc|c} j & j_1+1 & j_2-1 \\ m_j & -m_1 & m_2 \end{array}\right) \sqrt{(j_1+1)^2 - m_1} \\
&= -\sqrt{j^2 - m_j^2}\, \frac{E(j, j_1, j_2-1)}{2j(2j+1)} \left(\begin{array}{cc|c} j-1 & j_1 & j_2-1 \\ m_j & -m_1 & m_2 \end{array}\right) \\
&\quad+ m_j \frac{F(j, j_1, j_2-1)}{2j(j+1)} \left(\begin{array}{cc|c} j & j_1 & j_2-1 \\ m_j & -m_1 & m_2 \end{array}\right) \\
&\quad+ \sqrt{(j+1)^2 - m_j^2}\, \frac{C(j, j_1, j_2-1)}{2(j+1)(2j+1)} \left(\begin{array}{cc|c} j+1 & j_1 & j_2-1 \\ m_j & -m_1 & m_2 \end{array}\right)
\end{aligned} \tag{31}$$

Quantities E, F and C are defined in the appendix.

The rigorous derivation including all the details of recurrent procedure is very tedious and need not be given here (see Ref. [13]). Using the orthonormality condition for the Clebsch–Gordon coefficients [13], we obtain ultimately

$$\langle j_1+1,\, j_2-1,\, j,\, l\,|\cos\theta_{12}|\,j_1, j_2, j, l\rangle$$
$$=\frac{1}{2}\left(\frac{[(j_1+1)^2-k_1^2](j_2^2-k_2^2)[j^2-(j_1-j_2+1)^2][(j+1)^2-(j_1-j_2+1)^2]}{j_2^2(4j_2^2-1)(j_1+1)^2(2j_1+3)(2j_1+1)}\right)^{1/2}. \tag{32}$$

It is seen that a very complicated integral (25) is now transformed into a simple analytical form. Therefore, estimation of the matrix elements defined in Eq. (22) imposes minimal demands on computer memory and cpu time.

All the integrals that appear in our calculations are given in the appendix. Derivation is onerous but conceptually easy. All the expressions are general and are not restricted to our system. For instance, in the system ion–dipole (two-dimensional rotor) we can substitute $j'=j_1'$, $j_2=0$, $j=j_1$, $k_1=0$ and $k_2=0$. For $j_1'=j_1\pm 1$ and $l'=l\pm 1$ we obtain integrals of the form $\langle j_1', l', J\,|\cos\theta_1|\,j_1, l, J\rangle$ in perfect agreement with the results reported earlier for this system [6].

Note that matrix elements (22) are independent of number M as a result of total momentum conservation in this system. However, if number M is to be cancelled, the forces connected with the V potential must be strictly Newtonian, i.e. obeying the principle of equal action and reaction. For this reason the angle relations in the V potential must not be selected arbitrarily (for instance, simplification in Eq. (10) to the first term). Otherwise, the principle of total momentum conservation may be violated.

Finally, the matrix elements are obtained as the sums of the integral products evaluated in the appendix. For instance,

$$-\varepsilon_1(\psi_n^{(0)}, \cos^2\theta_1\psi_m^{(0)})-\varepsilon_2(\psi_n^{(0)}, \cos^2\theta_2\psi_m^{(0)})$$
$$=-\varepsilon_1\sum_{j_1''}\sum_{j''}\sum_{l''}\langle j_1'', j'', l''\,|\cos\theta_1|\,j_1, j, l\rangle\langle j_1', j', l'\,|\cos\theta_1|\,j_1'', j,''\, l''\rangle$$
$$-\varepsilon_2\sum_{j_2''}\sum_{j''}\sum_{l''}\langle j_2'', j'', l''\,|\cos\theta_2|\,j_2, j, l\rangle\langle j_2', j', l'\,|\cos\theta_2|\,j_2'', j,''\, l''\rangle, \tag{33}$$

Table 2. Representative values for the matrix elements $r=4.0$ Å, $n\equiv\{j_1=3, j_2=4, j=5, l=5, J=7, k_1=2, k_2=2\}$

Set "m"	$V_{mm}\times 10^2$ [kcal/mol	$V_{nm}\times 10^2$ [kcal/mol]
$j_1-1, j_2-2, j-4, l+2$	−3.097	0.3522
$j_1-1, j_2-2, j-3, l+4$	−6.031	0.0403
$j_1-1, j_2-2, j-3, l$	−5.556	−0.3417
$j_1-1, j_2, j-2, l+2$	−4.272	−0.5952
j_1-1, j_2, j, l	−4.732	0.7558
j_1, j_2-2, j, l	−5.974	−0.2355
$j_1, j_2, j-1, l-2$	−5.117	−0.2577
$j_1, j_2, j-1, l$	−4.904	0.0298
j_1, j_2, j, l	−4.809	−4.809
$j_1+1, j_2+2, j+1, l-4$	−5.076	−0.1375

where the summation limits are as follows: $j_1 - 1 \leqslant j_1'' \leqslant j_1 + 1$; $j_2 - 1 \leqslant j_2'' \leqslant j_2 + 1$; $j - 1 \leqslant j'' \leqslant j + 1$; $l'' = l \pm 1$. The remaining part of V_{nm} is transformed into the similar form. Representative results are listed in Table 2. As the V_{nm} elements are on the average smaller than V_{nn} (or V_{mm}) ones by an order of magnitude we can write

$$|(\psi_n^{(0)}, \hat{H}'\psi_n^{(0)})| \gg |(\psi_n^{(0)}, \hat{H}'\psi_m^{(0)})|. \tag{34}$$

4 Evaluation of the energy levels

At long distances, longer than about 5 Å, $\hat{H}'$ becomes a very small perturbation with respect to $\hat{H}_J^{(0)}$. Simple Rayleigh–Schrödinger perturbation calculus can be used under such circumstances. However, restriction to so long distances puts severe limitations on the amount of information that can be gained.

What makes the matters worse, the simple perturbation calculus has other drawbacks. The energy levels are degenerated, for instance, with respect to the number j. Moreover, it can readily be shown that the spectrum of zero-point energies includes the states infinitely close to each other; this leads to similar difficulties as does degeneration.

Apparently, more sophisticated methods are needed to approximate solutions of Eq. (2). The Brillouin–Wigner series [9] offers a promising option. This method yields the energy levels as the function [9]

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + E_n^{(3)} + \cdots, \tag{35}$$

where zero-point energies $E_n^{(0)}$ are defined in Eq. (20) while other terms are given below:

$$E_n^{(1)} = (\psi_n^{(0)}, \hat{H}'\psi_n^{(0)}), \tag{36}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{|(\psi_n^{(0)}, \hat{H}'\psi_m^{(0)})|^2}{E_n - E_m^{(0)}}, \tag{37}$$

$$E_n^{(3)} = \sum_{m' \neq n} \sum_{m \neq n} \frac{(\psi_n^{(0)}, \hat{H}'\psi_{m'}^{(0)})(\psi_{m'}^{(0)}, \hat{H}'\psi_m^{(0)})(\psi_n^{(0)}, \hat{H}'\psi_m^{(0)})}{(E_n - E_m^{(0)})(E_n - E_{m'}^{(0)})}. \tag{38}$$

Note that the components of function (35) are not simple equivalents to the corrections in the Rayleigh–Schrödinger series and exhibit quite a different form.

As the unknown E_n appears both on the left- and right-hand sides of Eq. (35), the mathematical formalism is more complicated than for the simple Rayleigh–Schrödinger calculus. On the other hand, the E_n level does not correspond to any of the $E_m^{(0)}$ levels; all the problems with the degenerated and too close states disappear.

To assess at what range is Eq. (35) valid we substitute as the first approximation on the right-hand side,

$$E_{n(1)} = E_n^{(0)} + E_n^{(1)}. \tag{39}$$

For the degenerated and close states the following condition has to be obeyed

$$|E_n^{(1)}| \gg |V_{nm}|. \tag{40}$$

As already mentioned such a condition is indeed obeyed over the range $r > 3.5$ Å, as $E_n^{(1)}$ is generally rather large in our system. The negative sign of the first correction term is also of importance. For the very typical case which features $E_m^{(0)} > E_n^{(0)}$, the condition to be obeyed transforms into

$$|E_n^{(1)}| + |E_m^{(0)} - E_n^{(0)}| \gg |V_{nm}|. \tag{41}$$

Since the contribution from $E_n^{(1)}$ overwhelms decisively the contributions from further expansion terms, $E_n^{(2)}$ and $E_n^{(3)}$, the Brillouin–Wigner series can encompass much wider range of levels than can the Rayleigh–Schrödinger calculus. The higher rotational states typical for higher temperatures are of foremost interest. It follows from Eq. (41) that our calculations are the more accurate the larger the differences $|E_m^{(0)} - E_n^{(0)}|$ and, consequently, the higher the rotational levels.

Iterations are needed, however, to obtain desired accuracy. Series (35) is the function of the type $E_n = f(E_n)$. First approximation yields $E_{n(2)} = f(E_{n(1)})$, followed by $E_{n(3)} = f(E_{n(2)})$, etc. Repetition continues until accuracy is found to be satisfactory. If convergence is to be achieved and a unique solution found, the Banach principle [14] has to be obeyed at every ith iteration step

$$\left|\frac{f(E_{n(i+1)}) - f(E_{n(i)})}{E_{n(i+1)} - E_{n(i)}}\right| < 1. \tag{42}$$

It puts important restriction on the procedure, as the first approximation has to be in the vicinity of the sought zero E_n value. If processes are divergent, a proper zero value cannot be singled out.

Unfortunately, divergent solutions abound in our calculations especially at small distances r and low energies $E_n^{(0)}$. Some happen at higher levels as well. However, if the contribution of the higher terms $E_n^{(2)}$ and $E_n^{(3)}$ does not exceed about 20%, the first substitution can suffice.

The detailed form for sum (37) is

$$E_n^{(2)} = \sum_{j_1'}\sum_{j_2'}\sum_{j'}\sum_{l'}{}' \frac{|\langle j_1', j_2', j', l' | \hat{H}' | j_1, j_2, j, l\rangle|^2}{E_n - E^{(0)}_{j_1', j_2', l', k_1, k_2}}, \tag{43}$$

where the limits of summation are: $j_1 - 2 \leqslant j_1' \leqslant j_1 + 2$; $j_1 - 2 \leqslant j_2' \leqslant j_2 + 2$; $j - 4 \leqslant j' \leqslant j + 4$; $l - 4 \leqslant l' \leqslant l + 4$. The subscript prime denotes the discarding of the component $m = n$. Other sums are written likewise.

Representative results are shown in Table 3. The values for $E_n^{(2)}$ and $E_n^{(3)}$ are closely interlinked with each other. The $E_n^{(3)}$ term is estimated depending on the needs and time available for computing. $E_n^{(2)}$ and $E_n^{(3)}$ are usually but not always negative.

The kinetic and potential parts can be singled out in $E_n(r)$,

$$E_n(r) = E^{(0)}_{j_1, k_1} + E^{(0)}_{j_2, k_2} + \frac{\hbar^2}{2\mu r^2} l(l+1) + U_n(r), \tag{44}$$

where the first two components depict the kinetic energy of the intrinsic rotational motion of radicals, the third component is the centrifugal potential of the orbital motion, and the fourth component is the potential energy along r given by

$$U_n(r) = \varepsilon_0 + E_n^{(1)} + E_n^{(2)} + E_n^{(3)}. \tag{45}$$

Equation (44) is very helpful in the analysis of motion of reacting systems.

Table 3. Selected values for the series (35) (distance r in Å, energies in kcal/mol)

r	$E_n^{(0)}$	$E_n^{(1)}$	$E_n^{(2)}$	$E_n^{(3)}$	E_n	$\langle E_n \rangle$
$j_1=1$	$j_2=1$	$j=2$	$l=3$	$J=1$	$k_1=0$	$k_2=0$
3.7	−0.0975	−0.3036	−0.1242	−0.1083	−0.6336	−0.3279
4.0	−0.0817	−0.0932	−0.0395	−0.0302	−0.3445	−0.2500
4.2	−0.1677	−0.0338	−0.0174	−0.0126	−0.2315	−0.1916
4.5	−0.1180	0.0025	0.0036	0.0011	−0.1108	−0.1150
$j_1=2$	$j_2=3$	$j=2$	$l=30$	$J=30$	$k_1=2$	$k_2=2$
3.5	0.8964	−0.3175	−0.2454		0.3335	0.4274
3.7	0.6091	−0.1536	−0.1440		0.3115	0.3787
4.0	0.4627	−0.0420	−0.0077		0.4130	0.3944
4.2	0.4424	−0.0115	−0.0033		0.4275	0.4187
4.5	0.4491	0.0062	0.0005		0.4557	0.4520
$j_1=10$	$j_2=10$	$j=15$	$l=10$	$J=20$	$k_1=5$	$k_2=0$
3.5	5.804	−0.3353	0.0447		5.514	5.335
3.7	5.562	−0.1625	−0.0123		5.388	5.332
4.0	5.472	−0.0447	−0.0084		5.418	5.403
4.2	5.482	−0.0125	0.0032		5.473	5.458
4.5	5.527	0.0062			5.533	5.529

Once the energy level E_n is known, its wave function can be estimated [9] as

$$\psi_n^{\mathrm{JM}} = \psi_n^{(0)} + \sum_{m \neq n} \frac{(\psi_n^{(0)}, \hat{H}'\psi_m^{(0)})}{E_n - E_m^{(0)}} + \cdots . \tag{46}$$

Evaluating averages note that function (46) is not normalized.

5 Conclusions

The Brillouin–Wigner series is a unique self-consistent variant of the perturbation calculus. Its features can be used to advantage but only upon the proviso that conditions (40) and (41) are obeyed. For instance, if the first term $E_n^{(1)}$ vanishes, the use of Brillouin–Wigner series offers no improvement compared with the simple Rayleigh–Schrödinger series.

The convergence of series (35) with inclusion of successive terms, $E_n^{(3)}$, $E_n^{(4)}$, etc., is a problem in itself, beyond the scope of this paper. Some comments are in order, however, to support our results. As we are concerned with higher energies and temperatures, the procedure similar to that described by Margenau and Kestler [15] can be used. The angle dependencies in the V potential are replaced by their averages obtained by integration over the full spherical angle and divided by 4π. We obtain $\langle \cos^2\theta_1 \rangle \equiv \langle \cos^2\theta_2 \rangle \equiv \langle \cos^2\theta_{12} \rangle = \frac{1}{3}$ and $\langle \cos\theta_1 \rangle = 0$, etc. The Schrödinger equation (2) can then be solved rigorously yielding the mean value for the energy, $\langle E_n \rangle$. Representative results are shown in Table 3. It is seen that only for the lowest states does $\langle E_n \rangle$ deviate markedly from E_n reaching as large a deviation as 20%. The higher the state the lower the difference, dwindling to only 2–3% for the highest rotational states.

It should be emphasized that only the general idea is outlined in this work. Many details are omitted, as, for instance, the problem how and when to evaluate $E_n^{(3)}$ and some others. Dealing with different systems one cannot find ready for use recipies of E_n estimation. Every case is unique.

It can be claimed that the aim of this work as given in Introduction has been achieved. The estimated $E_n(r)$ levels are numerous and accurate enough to offer considerable insight into the dynamics of interacting system. The weakness of the procedure, such as divergence for some of the states, can be alleviated by using special methods such as interpolation.

The results obtained in this paper are used extensively in the study on the rate of methyl radical recombination at higher pressures and temperatures [11].

Appendix

The integrals used for the estimation of matrix elements are calculated as follows: Firstly, the expressions are defined:

$$A(a,b,c)=\sqrt{(-a+b+c+1)(a-b+c)(a+b-c)(a+b+c+1)}, \tag{A1}$$

$$B(a,b,c)=a(a+1)+b(b+1)-c(c+1), \tag{A2}$$

$$C(a,b,c)=\sqrt{(-a+b+c)(-a+b+c+1)(a-b+c)(a-b+c+1)}, \tag{A3}$$

$$D(a,b,c)=\sqrt{(-a+b+c)(a-b+c+1)(a+b-c)(a+b+c+1)}, \tag{A4}$$

$$E(a,b,c)=\sqrt{(a+b-c)(a+b-c+1)(a+b+c+1)(a+b+c+2)}, \tag{A5}$$

$$F(a,b,c)=\sqrt{(-a+b+c+1)(a-b+c)(a+b-c+1)(a+b+c+2)}. \tag{A6}$$

If the terms of the type $1/j_1 j$ are present in some integrals, this integral retains meaning only at $j_1>0$ and $j>0$.

1. Integrals $\langle j_1', j_2', j', l' \,|\cos\theta_1|\, j_1, j_2, j, l\rangle$.

$$\langle j_1-1, j_2, j-1, l-1 \,|\cos\theta_1|\, j_1, j_2, j, l\rangle$$
$$=-\frac{1}{4}\frac{\sqrt{j_1^2-k_1^2}}{j_1\sqrt{(2j_1+1)(2j_1-1)}}\,\frac{E(j-1,j_1,j_2)}{j\sqrt{(2j+1)(2j-1)}}\,\frac{E(l-1,j,J)}{\sqrt{(2l+1)(2l-1)}}, \tag{A7}$$

$$\langle j_1, j_2, j-1, l-1 \,|\cos\theta_1|\, j_1, j_2 j, l\rangle$$
$$=-\frac{1}{4}\frac{k_1}{j_1(j_1+1)}\,\frac{A(j,j_1,j_2)}{j\sqrt{(2j+1)(2j-1)}}\,\frac{E(l-1,j,J)}{\sqrt{(2l+1)(2l-1)}}, \tag{A8}$$

$$\langle j_1+1, j_2, j-1, l-1 \,|\cos\theta_1|\, j_1, j_2, j, l\rangle$$

$$= \frac{1}{4} \frac{\sqrt{(j_1+1)^2 - k_1^2}}{(j_1+1)\sqrt{(2j_1+1)(2j_1+3)}} \frac{C(j-1, j_1, j_2)}{j\sqrt{(2j+1)(2j-1)}} \frac{E(l-1, j, J)}{\sqrt{(2l+1)(2l-1)}} \tag{A9}$$

$$\langle j_1 - 1, j_2, j, l-1 \,|\cos\theta_1|\, j_1, j_2, j, l\rangle$$

$$= \frac{1}{4} \frac{\sqrt{j_1^2 - k_1^2}}{j_1\sqrt{(2j_1+1)(2j_1-1)}} \frac{D(j, j_1, j_2)}{j(j+1)} \frac{A(l, j, J)}{\sqrt{(2l+1)(2l-1)}} \tag{A10}$$

$$\langle j_1, j_2, j, l-1 \,|\cos\theta_1|\, j_1, j_2, j, l\rangle$$

$$= -\frac{1}{4} \frac{k_1}{j_1(j_1+1)} \frac{B(j, j_1, j_2)}{j(j+1)} \frac{A(l, j, J)}{\sqrt{(2l+1)(2l-1)}}, \tag{A11}$$

$$\langle j_1 + 1, j_2, j, l-1 \,|\cos\theta_1|\, j_1, j_2, j, l\rangle$$

$$= \frac{1}{4} \frac{\sqrt{(j_1+1)^2 - k_1^2}}{(j_1+1)\sqrt{(2j_1+1)(2j_1+3)}} \frac{F(j, j_1, j_2)}{j(j+1)} \frac{A(l, j, J)}{\sqrt{(2l+1)(2l-1)}} \tag{A12}$$

$$\langle j_1 - 1, j_2, j+1, l-1 \,|\cos\theta_1|\, j_1, j_2, j, l\rangle$$

$$= -\frac{1}{4} \frac{\sqrt{j_1^2 - k_1^2}}{j_1\sqrt{(2j_1+1)(2j_1-1)}} \frac{C(j+1, j_1, j_2)}{(j+1)\sqrt{(2j+1)(2j+3)}} \frac{C(l-1, j, J)}{\sqrt{(2l+1)(2l-1)}} \tag{A13}$$

$$\langle j_1, j_2, j+1, l-1 \,|\cos\theta_1|\, j_1, j_2, j, l\rangle$$

$$= \frac{1}{4} \frac{k_1}{j_1(j_1+1)} \frac{A(j+1, j_1, j_2)}{(j+1)\sqrt{(2j+1)(2j+3)}} \frac{C(l-1, j, J)}{\sqrt{(2l+1)(2l-1)}} \tag{A14}$$

$$\langle j_1 + 1, j_2, j+1, l-1 \,|\cos\theta_1|\, j_1, j_2, j, l\rangle$$

$$= \frac{1}{4} \frac{\sqrt{(j_1+1)^2 - k_1^2}}{(j_1+1)\sqrt{(2j_1+1)(2j_1+3)}} \frac{E(j+1, j_1, j_2)}{(j+1)\sqrt{(2j+1)(2j+3)}} \frac{C(l-1, j, J)}{\sqrt{(2l+1)(2l-1)}} \tag{A15}$$

$$\langle j_1 - 1, j_2, j-1, l+1 \,|\cos\theta_1|\, j_1, j_2, j, l\rangle$$

$$= \frac{1}{4} \frac{\sqrt{j_1^2 - k_1^2}}{j_1\sqrt{(2j_1+1)(2j_1-1)}} \frac{E(j-1, j_1, j_2)}{j\sqrt{(2j+1)(2j-1)}} \frac{C(l+1, j, J)}{\sqrt{(2l+1)(2l+3)}} \tag{A16}$$

$$\langle j_1, j_2, j-1, l+1 \,|\cos\theta_1|\, j_1, j_2, j, l\rangle$$

$$= \frac{1}{4} \frac{k_1}{j_1(j_1+1)} \frac{A(j, j_1, j_2)}{j\sqrt{(2j+1)(2j-1)}} \frac{C(l+1, j, J)}{\sqrt{(2l+1)(2l+3)}} \tag{A17}$$

$$\langle j_1 + 1, j_2, j-1, l+1 \,|\cos\theta_1|\, j_1, j_2, j, l\rangle$$

$$= -\frac{1}{4}\frac{\sqrt{(j_1+1)-k_1^2}}{(j_1+1)\sqrt{(2j_1+1)(2j_1+3)}}\frac{C(j-1,j_1,j_2)}{j\sqrt{(2j+1)(2j-1)}}\frac{C(l+1,j,J)}{\sqrt{(2l+1)(2l+3)}} \tag{A18}$$

$$\langle j_1-1,j_2,j,l+1\,|\cos\theta_1|\,j_1,j_2,j,l\rangle$$

$$=\frac{1}{4}\frac{\sqrt{j_1^2-k_1^2}}{j_1\sqrt{(2j_1+1)(2j_1-1)}}\frac{D(j,j_1,j_2)}{j(j+1)}\frac{F(J,l,j)}{\sqrt{(2l+1)(2l+3)}} \tag{A19}$$

$$\langle j_1,j_2,j,l+1\,|\cos\theta_1|\,j_1,j_2,j,l\rangle$$

$$= -\frac{1}{4}\frac{k_1}{j_1(j_1+1)}\frac{B(j,j_1,j_2)}{j(j+1)}\frac{F(J,l,j)}{\sqrt{(2l+1)(2l+3)}} \tag{A20}$$

$$\langle j_1+1,j_2,j,l+1\,|\cos\theta_1|\,j_1,j_2,j,l\rangle$$

$$=\frac{1}{4}\frac{\sqrt{(j_1+1)^2-k_1^2}}{(j_1+1)\sqrt{(2j_1+1)(2j_1+3)}}\frac{F(j,j_1,j_2)}{j(j+1)}\frac{F(J,l,j)}{\sqrt{(2l+1)(2l+3)}} \tag{A21}$$

$$\langle j_1-1,j_2,j+1,l+1\,|\cos\theta_1|\,j_1,j_2,j,l\rangle$$

$$=\frac{1}{4}\frac{\sqrt{j_1^2-k_1^2}}{j_1\sqrt{(2j+1)(2j_1-1)}}\frac{C(j+1,j_1,j_2)}{(j+1)\sqrt{(2j+1)(2j+3)}}\frac{E(l,j+1,J)}{\sqrt{(2l+1)(2l+3)}} \tag{A22}$$

$$\langle j_1,j_2,j+1,l+1\,|\cos\theta_1|\,j_1,j_2,j,l\rangle$$

$$= -\frac{1}{4}\frac{k_1}{j_1(j_1+1)}\frac{A(j+1,j_1,j_2)}{(j+1)\sqrt{(2j+1)(2j+3)}}\frac{E(l,j+1,J)}{\sqrt{(2l+1)(2l+3)}} \tag{A23}$$

$$\langle j_1+1,j_2,j+1,l+1\,|\cos\theta_1|\,j_1,j_2,j,l\rangle$$

$$= -\frac{1}{4}\frac{\sqrt{(j_1+1)^2-k_1^2}}{(j_1+1)\sqrt{(2j_1+1)(2j_1+3)}}\frac{E(j+1,j_1,j_2)}{(j+1)\sqrt{(2j+1)(2j+3)}}\frac{E(l,j+1,J)}{\sqrt{(2l+1)(2l+3)}}. \tag{A24}$$

All other integrals are zero.

2. Integrals $\langle j_1',j_2',j',l'\,|\cos\theta_2|\,j_1,j_2,j,l\rangle$:
   Estimation is based on the symmetry

$$\langle j_1',j_2',j',l'\,|\cos\theta_2|\,j_1,j_2,j,l\rangle$$

$$= -(-1)^{j_2'+j'+l'-j_2-j-1}\langle j_2',j_1',j',l'\,|\cos\theta_2|\,j_2,j_1,j,l\rangle. \tag{A25}$$

For example,

$$\langle j_1,j_2-1,j,l-1\,|\cos\theta_2|\,j_1,j_2 j,l\rangle = -\langle j_2-1,j_1,j,l-1\,|\cos\theta_2|\,j_2,j_1,j,l\rangle \tag{A26}$$

On the basis of Eq. (A10) we obtain

$$\langle j_1, j_2 - 1, j, l - 1 \,|\cos\theta_2|\, j_1, j_2, j, l\rangle$$

$$= -\frac{1}{4}\frac{\sqrt{j_2^2 - k_2^2}}{j_2\sqrt{(2j_2+1)(2j_2-1)}}\,\frac{D(j, j_2, j_1)}{j(j+1)}\,\frac{A(l, j, J)}{\sqrt{(2l+1)(2l-1)}} \tag{A27}$$

and so forth.

3. Integrals $\langle j_1', j_2', j', l' \,|\cos\theta_{12}|\, j_1, j_2, j, l\rangle$.

$$\langle j_1, j_2, j, l \,|\cos\theta_{12}|\, j_1, j_2, j, l\rangle$$

$$= \frac{1}{2}\frac{k_1 k_2}{2 j_1(j_1+1) j_2(j_2+1)}[j(j+1) - j_1(j_1+1) - j_2(j_2+1)] \tag{A28}$$

$$\langle j_1 - 1, j_2, j, l \,|\cos\theta_{12}|\, j_1, j_2, j, l\rangle$$

$$= -\frac{1}{2}k_2\left(\frac{(j_1^2 - k_1^2)[j_1^2 - (j - j_2)^2][(j + j_2 + 1)^2 - j_1^2]}{j_1^2(4j_1^2 - 1) j_2^2 (j_2 + 1)^2}\right)^{1/2} \tag{A29}$$

$$\langle j_1, j_2 - 1, j, l \,|\cos\theta_{12}|\, j_1, j_2, j, l\rangle$$

$$= \frac{1}{2}k_1\left(\frac{(j_2^2 - k_2^2)[j_2^2 - (j - j_1)^2][(j + j_1 + 1)^2 - j_2^2]}{j_2^2(4j_2^2 - 1) j_1^2 (j_1 + 1)^2}\right)^{1/2} \tag{A30}$$

$$\langle j_1 + 1, j_2, j, l \,|\cos\theta_{12}|\, j_1, j_2, j, l\rangle$$

$$= -\frac{1}{2}k_2\left(\frac{[(j_1+1)^2 - k_1^2][(j_1+1)^2 - (j - j_2)^2][(j + j_2 + 1)^2 - (j_1+1)^2]}{(2j_1+3)(2j_1+1)(j_1+1)^2 j_2^2 (j_2+1)^2}\right)^{1/2} \tag{A31}$$

$$\langle j_1, j_2 + 1, j, l \,|\cos\theta_{12}|\, j_1, j_2, j, l\rangle$$

$$= \frac{1}{2}k_1\left(\frac{[(j_2+1)^2 - k_2^2][(j_2+1)^2 - (j - j_1)^2][(j + j_1 + 1)^2 - (j_2+1)^2]}{(2j_2+3)(2j_2+1)(j_2+1)^2 j_1^2 (j_1+1)^2}\right)^{1/2} \tag{A32}$$

$$\langle j_1 + 1, j_2 - 1, j, l \,|\cos\theta_{12}|\, j_1, j_2, j, l\rangle$$

$$= \frac{1}{2}\left(\frac{[(j_1+1)^2 - k_1^2][j_2^2 - k_2^2][j^2 - (j_1 - j_2 + 1)^2][(j+1)^2 - (j_1 - j_2 + 1)^2]}{j_2^2(4j_2^2 - 1)(j_1+1)^2(2j_1+3)(2j_1+1)}\right)^{1/2} \tag{A33}$$

$$\langle j_1 - 1, j_2 + 1, j, l \,|\cos\theta_{12}|\, j_1, j_2, j, l\rangle$$

$$= \frac{1}{2}\left(\frac{[(j_2+1)^2 - k_2^2][j_1^2 - k_1^2][j^2 - (j_2 - j_1 + 1)^2][(j+1)^2 - (j_2 - j_1 + 1)^2]}{j_1^2(4j_1^2 - 1)(j_2+1)^2(2j_2+3)(2j_2+1)}\right)^{1/2} \tag{A34}$$

$$\langle j_1 + 1, j_2 + 1, j, l \,|\cos\theta_{12}|\, j_1, j_2, j, l\rangle$$

$$= -\frac{1}{2}\left(\frac{[(j_1+1)^2-k_1^2][(j_2+1)^2-k_2][(j_1+j_2+2)^2-(j+1)^2][(j_1+j_2+2)^2-j^2]}{(2j_1+3)(2j_1+1)(j_1+1)^2(2j_2+3)(2j_2+1)(j_2+1)^2}\right)^{1/2} \tag{A35}$$

$$\langle j_1-1, j_2-1, j, l|\cos\theta_{12}|j_1, j_2, j, l\rangle$$

$$= -\frac{1}{2}\left(\frac{(j_1^2-k_1^2)(j_2^2-k_2^2)[(j_1+j_2)^2-j^2][(j_1+j_2)^2-(j+1)^2]}{j_1^2 j_2^2(4j_1^2-1)(4j_2^2-1)}\right)^{1/2} \tag{A36}$$

All other integrals are zero.

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